

Vitreous compositions of the vitroceramic type, transparent to infrared

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5 A subject matter of the invention is vitreous compositions, in particular of vitroceramic type, which are transparent in the infrared, their processes of preparation and their uses.

10 More specifically, the present invention is targeted at providing a material capable of ensuring the transmission of infrared radiation, that is to say having a transparency in the wavelengths extending from 0.7 to 14 μm and in particular extending from 0.7 to 11 μm or from 0.9 to 14 μm . Such materials are used in the field
15 of thermal imaging and in particular for the manufacture of optical components for infrared systems, such as, for example, thermal imagers.

20 Monocrystalline germanium currently composes the majority of the optics of infrared cameras. Unfortunately, it is a rare and expensive material, the forming of which is lengthy and expensive.

25 More recently, glasses transparent in the infrared have been proposed as an alternative to monocrystalline germanium. Mention may be made, as representative of these transparent glasses, of chalcogenide glasses, in particular vitreous compositions based on gallium, on germanium and on antimony, and more particularly those
30 disclosed in patent EP 1 034 145. However, although satisfactory in terms of transparency in the infrared and of cost, such glasses generally have a limited resistance to mechanical impacts and thermal shocks.

35 Furthermore, it is known to obtain, from certain glasses, materials of vitroceramic type which combine advantages of ceramics (high hardness, good mechanical properties, low thermal expansion) and advantages of

glasses (ease of manufacture, forming). These materials are obtained as the result of a heat treatment of certain vitreous compositions, so as to bring about their partial crystallization. Thus, vitroceramics
5 based on oxides, the main constituents of which are generally SiO_2 and/or Al_2O_3 , are already disclosed in the documents US 4 835 121 and US 2002/0022564. However, these vitroceramics are not transparent in the infrared for wavelengths greater than at most 4 μm ,
10 which is inadequate for a great many applications.

Finally, there also exist ceramics, transparent to infrared radiation, based on ZnS or ZnSe nanocrystals. Unfortunately, the preparation and the forming of these
15 ceramics are complex.

Consequently, there remains to this day a need for a material which makes it possible to simultaneously satisfy all the abovementioned requirements, namely
20 transparency in the infrared, in particular in the wavelengths between 0.7 and 14 μm , low cost and good thermal/mechanical properties.

Surprisingly, the inventors have discovered that it is
25 possible to obtain vitroceramics of chalcogenide type which exhibit transparency in the infrared.

More specifically, the invention relates mainly to a composition of vitroceramic type comprising, in mol%:
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Ge	5-40
Ga	< 1
S + Se	40-85
Sb + As	4-40
MX	2-25
Ln	0-6
Adjuvant	0-30

in which:

- M represents at least one alkali metal chosen in particular from Rb, Cs, Na, K and Zn,
- X represents at least one chlorine, bromine or iodine atom,
- 5 - Ln represents at least one rare earth metal, and
- Adjuvant represents at least one additive composed of at least one metal and/or at least one metal salt,

with the sum of the combination of the molar percentages of the components present in said composition being equal to 100.

According to a specific alternative form, the content of antimony and/or arsenic can vary from 5 to 40 mol%.

15 According to a favored alternative form of the invention, this composition is a vitroc ceramic which is transparent in the infrared, in particular in the wavelengths extending from 0.7 to 14 μm and especially
20 extending from 0.7 to 11 μm or from 0.9 to 14 μm . To be specific, the transparency of these vitroc ceramic compositions can in particular be adjusted, according in particular to the nature of their components, to one of the ranges extending from 0.7 to 11 μm or from 0.9
25 to 14 μm .

Advantageously, the vitroc ceramic compositions according to the invention thus prove to be transparent in the operating ranges commonly selected for thermal imagers,
30 that is to say the ranges of wavelengths extending from 3 to 5 μm and from 8 to 12 μm .

In some cases, optical losses due to the crystals present in the composition may be recorded in the short
35 wavelengths typically extending from 0.6 to 2 μm . However, they have no significant effect in the ranges of wavelengths extending from 3 to 5 μm and from 8 to 12 μm .

Said vitroceraamic compositions according to the invention can be obtained by specific heat treatment of vitreous compositions with the same composition but devoid of crystals, also referred to as "non-crystalline".

Within the meaning of the present invention, a vitreous composition is regarded as noncrystalline from the moment when it does not diffract X-rays and when observation under an electron microscope does not reveal crystals.

These vitreous compositions, i.e. noncrystalline compositions, constitute another subject matter of the invention. Due to their composition, they advantageously make it possible to obtain, via an appropriate heat treatment, nucleation and crystalline growth which are controlled so as to be compatible with an application in infrared and to confer the expected mechanical and thermal properties on the corresponding vitroceraamic compositions.

Thus, the appropriate heat treatment applied to these vitreous compositions is such that it makes it possible to generate crystals, observable under an electron microscope, with a size of less than 1 μm in the vitroceraamic thus obtained.

These crystals generally have a size of less than 1 μm , in particular of less than or equal to 500 nm, especially of less than or equal to 400 nm, indeed even of less than or equal to 300 nm.

They can exhibit a size of greater than or equal to 1 nm, in particular of greater than or equal to 2 nm, especially of greater than or equal to 5 nm, indeed even of greater than or equal to 10 nm.

More particularly, these crystals exhibit a size

varying from 10 to 300 nm and in particular from 50 to 300 nm.

5 The size and the distribution of the crystals can be observed by observation with an electron microscope.

10 In particular, the chalcogenide vitroceramics according to the invention can comprise at least 0.1% of crystallized volume with crystals with a size of less than or equal to 1 μm and in particular of less than or equal to 400 μm . However, it is clear that this amount by volume of crystals can be adjusted and in particular increased, according to the applications envisaged. By way of example, for optical amplification, 0.1% of
15 crystallized rare earth metal ions may be more than sufficient. On the other hand, a level of crystallized volume of greater than 10%, 40%, indeed even more, will for its part be more particularly advantageous in reducing the coefficient of expansion of a composite
20 material.

These values of percentage of crystallized volume can be observed by observation under an electron microscope.

25 According to a specific alternative form, the compositions according to the invention comprise gallium in a content of less than or equal to 0.75 mol%, in particular in a content of less than or equal to 0.5 mol%, especially in a content of less than or equal to
30 0.25 mol%, indeed even in a content of less than or equal to 0.1 mol%.

More particularly, the compositions according to the invention are devoid of gallium. The term "devoid of
35 gallium" is understood to mean a content at most equal to the content of gallium present as impurity in the other components.

The compositions according to the invention comprise

germanium in a content which can in particular vary from 10 to 35 mol%.

5 Likewise, they comprise sulfur and/or selenium in a content which can vary in particular from 45 to 75 mol% and especially from 50 to 75 mol%.

10 The compositions according to the invention comprise antimony and/or arsenic in a content which can vary in particular from 4 to 25 mol% and especially from 8 to 20 mol%.

15 As regards the compound MX, it is chosen more particularly from CsCl, CsBr, CsI, NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbBr, RbI, ZnCl₂, ZnBr₂ and ZnI₂ and in particular from ZnCl₂, CsCl, CsBr, CsI and their mixtures. This compound MX is generally present in a content varying in particular from 2 to 15 mol%.

20 As regards the rare earth metal component, Ln, of the composition according to the invention, it can be chosen more particularly from Dy, Er, Nd, Pr, Yb, Tm, Ho and their mixtures. It is generally present in a content varying in particular from 0 to 3 mol%.

25 Of course, the compositions according to the invention are capable of comprising one or more adjuvants. As specified above, the adjuvant can be a metal, a metal salt or their mixtures.

30 According to a specific alternative form of the invention, these adjuvants can be chosen from calcium, barium, indium, tellurium, silver, copper, lead, cadmium, their salts, such as, for example, PbI₂ or 35 CuI, and their derivatives, such as, for example, Ag₂Se and CdTe, and their mixtures.

These adjuvants are generally present in particular in a proportion of from 0 to 10 mol%.

According to a specific alternative form, the compositions according to the invention are a quaternary mixture of germanium in a content varying from 15 to 30 mol%, of antimony in a content varying from 4 to 20 mol%, of selenium in a content varying from 50 to 70 mol% and of cesium halide, such as CsCl, CsBr or CsI, in a content varying from 3 to 15 mol%.

According to another specific alternative form, the compositions according to the invention are a quaternary mixture of germanium in a content varying from 15 to 20 mol%, of antimony in a content varying from 10 to 15 mol%, of sulfur in a content varying from 45 to 65 mol% and of cesium halide, such as CsCl, CsBr or CsI, in a content varying from 2 to 15 mol%.

According to yet another specific alternative form, the compositions according to the invention are a five-component mixture of germanium in a content extending from 10 to 25 mol%, of antimony in a content extending from 10 to 25 mol%, of selenium in a content extending from 55 to 65 mol%, of cesium halide, such as CsCl, CsBr or CsI, in a content extending from 2 to 5 mol% and of an adjuvant chosen from PbI_2 , CuI, Ag_2Se and CdTe in a content extending from 1 to 7 mol%.

As specified above, the vitroc ceramic composition can be obtained as the result of a heat treatment of a vitreous composition according to the invention. This heat treatment can last from one hour to one month, indeed even more, and has to be carried out at a temperature greater than the glass transition temperature (T_g) of the vitreous composition, so as to generate crystals compatible in number and in size with transparency in the infrared, particularly in the wavelengths extending from 0.7 to 14 μm and in particular extending from 0.7 to 11 μm or from 0.9 to 14 μm .

As regards these noncrystalline vitreous (or nonvitro-ceramic) compositions according to the invention, they can be obtained by a preparation process comprising in particular the stages consisting in:

- introducing the germanium, the gallium, the sulfur and/or the selenium, the antimony and/or the arsenic, Ln and the adjuvant, in the desired proportions, into a tube of silica, in particular,
- pumping under vacuum, for example down to 10^{-4} mbar, and sealing said tubes of silica,
- bringing said tubes to temperatures varying from 700 to 1000°C,
- homogenizing the mixture at this temperature for a period of time of between 1 and 10 hours,
- rapidly cooling down to a temperature from 20 to 30°C below the glass transition temperature of said mixture, and
- slowly cooling said mixture down to ambient temperature.

This process for the manufacture of the vitreous composition according to the invention can additionally comprise a purification stage consisting in adding at most 500 ppm of at least one oxygen scavenger, such as, for example, aluminum, magnesium or their mixtures, before vacuum distillation of said vitreous composition.

The vitroceramics according to the invention can be used in an infrared system and in particular for manufacturing optics for any infrared system operating in particular from 0.7 to 14 μm and especially extending from 0.7 to 11 μm or from 0.9 to 14 μm , and especially from 3 to 5 μm and/or from 8 to 12 μm . In the case where they comprise rare earth metals, they can also be used for optical amplification.

Figure:

Figure 1 is a photograph at a magnification $\times 20\ 000$ of the chalcogenide vitroceramic having the composition described in example 3.

The following examples are given by way of illustration and in no way of limitation of the invention.

10 **Examples:**

Examples 1 to 47 presented below report 47 compositions of vitroceramic type in accordance with the invention.

15 By carrying out the operation as indicated above, vitreous compositions having the compositions specified below are prepared in a first step.

For the manufacture of the corresponding vitroceramics, these vitreous compositions are heated up to a temperature greater than their glass transition temperature (T_g) for a more or less lengthy period depending on the size and on the amount of crystals desired.

25 By way of example, for the vitreous composition No. 3, with a T_g of 260°C , the annealing is carried out at 290°C for a period of time typically varying from 1 hour to 1 month, which makes it possible to control the amount of crystals.

The vitroceramic thus obtained is illustrated by figure 1.

Examples	Ge	Sb	Se	CsCl
1	26.3	6.0	60.5	7.2
2	24.3	12.5	58.4	4.7
3	23.3	11.7	56	9.0
4	23.9	4.8	66.8	4.5
5	21.8	8.7	56.7	12.7
6	19.9	12.4	60.3	4.9

Examples	Ge	Sb	Se	CsBr
7	24.6	12.4	59.2	3.7
8	23.8	12.0	57.2	7
9	22.9	11.6	55.1	10.5
10	23.2	9.3	60.4	7.1
11	22.4	9.0	58.3	10.3
12	25.1	5.8	65.5	3.6
13	24.8	10.2	61.3	3.8

Examples	Ge	Sb	Se	CsI
14	24	12.4	57.5	6.0
15	23.3	11.8	56.1	8.8
16	24.6	5.6	64.0	5.8
17	22.8	9.1	59.4	8.6
18	24.8	10.8	61.4	3.1
19	19.9	16.3	60.7	3.1

Examples	Ge	Sb	S	CsCl
20	18.8	14.1	61.1	6
21	18.3	13.7	59.3	8.7
22	17.3	12.9	56.1	13.7
23	16.8	12.6	54.6	16

5

Examples	Ge	Sb	S	CsBr
24	19.5	14.6	63.4	2.5
25	18.6	13.9	60.4	7.0

Examples	Ge	Sb	S	CsI
26	19.2	14.4	62.4	4.0
27	18.5	13.9	60.0	7.6
28	16.0	12.0	52.1	6.6
29	15.4	11.5	49.9	6.3

Examples	Ge	Sb	Se	PbI ₂	CsI
30	21.9	12.9	60.3	2.5	2.4
31	15.1	18.3	58.3	6.2	2.1
32	17.1	17.2	60.9	2.8	2
33	13.4	20.9	60.9	2.7	2.1
34	20.2	14.3	61.8	1.5	2.2

Examples	Ge	Sb	Se	CuI	CsBr
35	19.3	12.9	59.7	6	2.1
36	21.2	11.8	61.6	3.1	2.3
37	16.2	17.3	60.1	4.2	2.2
38	11.8	23.2	60.5	2.5	2
39	17.4	15.8	59.2	5.1	2.5

Examples	Ge	Sb	Se	Ag ₂ Se	CsCl
40	16.2	18	60.3	3.5	2
41	21.2	12	61.7	3	2.1
42	12	22.6	60.9	2.5	2
43	21.7	13.2	60.5	2.4	2.2

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Examples	Ge	Sb	Se	CdTe	CsI
44	16.8	17.9	61.2	2.1	2
45	21.5	12.1	61.2	3	2.2
46	19	15.7	61.9	1.4	2
47	17.3	17.1	61	2.5	2.1

The intervals should be understood as limits included, unless otherwise specified.